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ENERGY SECURITY

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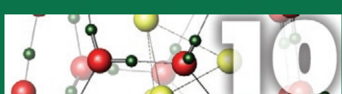
The Chemical Hydrogen Storage Center of Excellence. The promise of chemically bound hydrogen for on-board storage.



Caged Energy. Storing hydrogen in clathrates.

Superconducting Magnetic Energy Storage. Improved grid reliability, better integration of renewables, and cost-effective response to peak demand.

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Save it for a Rainy (or Windless, or Really Hot) Day

The importance of energy storage

"Make hay while the sun shines" and "save it for a rainy day": two old adages the electric power industry would be wise to follow, if only it could. The ability to generate energy at any time and bank it for later withdrawal would greatly enhance energy security by responding efficiently to demand variations (i.e., load leveling) and improving grid stability, reliability, and power quality. Energy storage technologies are also critical to greater integration of renewable energy sources by overcoming their biggest limitation—intermittency. The sun and the wind are not always in sync with consumer demand for electricity.

Some energy storage technologies are currently in use by utilities throughout the country (see table at right), but they have serious drawbacks, including excessive capital costs, geographical limitations, insufficient capacity, or toxicity. Cost-effective, widely applicable solutions have yet to enter the market. The Department of Energy's Office of Electricity Delivery and Energy Reliability names energy storage as one of six critical, crosscutting technologies that require intensive R&D to modernize the nation's energy delivery system and reduce system inefficiencies, greenhouse gas emissions, and dependence on foreign fuel sources.

Energy storage is not only crucial to grid modernization but also to the future of transportation. The top two contenders to power future

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The Challenge of Hydrogen Storage

The modern automobile represents the culmination of 100 years of research and development. It is reliable, inexpensive, and durable and, therefore, a formidable benchmark by which any alternative transportation system will be measured. The automobile owes much of its success to petroleum, which is unique in that it is both the energy source and the energy storage medium on

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Energy Storage: The State of the Art

TECHNOLOGY	HOW IT WORKS	USAGE IN U.S.
Pumped Hydroelectric	Off-peak electricity is used to pump water from a lower to a higher reservoir, then released downhill and passed through turbines during peak demand.	22 GW at 150 facilities in 19 states
Compressed Air Energy Storage	Off-peak electricity is used to compress air which is stored in underground caverns, then released through turbines during peak demand.	A 110 MW facility in Alabama
Utility Battery Storage	Various rechargeable batteries, mostly lead-acid and nickel-cadmium—others are under development.	70 MW used by utilities in 10 states
Superconducting Magnetic Energy Storage	Electricity is stored in a magnetic field created by the flow of direct current in a superconducting coil.	30 MW in 5 states
Flywheel Storage	Electricity is stored as inertial energy in a lightweight, low-friction flywheel spinning at high speed.	A small number of demonstration units
Hydrogen Energy Storage	Electricity produces hydrogen that is stored in gas, liquid, metal, or carbon-based form and converted back to electricity by a fuel cell or used directly.	Under development

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Los Alamos NATIONAL LABORATORY

Materials: An Enabler for Energy Security

Paul S. Follansbee
Division Director, Materials Science & Technology
Los Alamos National Laboratory

Boarding a commercial airplane today, I can't resist marveling at the materials technology advances that comprise the plane's engines. Modern air transportation is enabled by propulsion systems with increasing thrust levels and efficiencies. Materials evolutions fuel these advances. In particular, the advent of nickel-based superalloy airfoils, processing technologies yielding single crystal and directionally solidified grain structures, and adherent ceramic thermal barrier coatings all allow increased engine operating temperatures, with surface temperatures of the hottest, stressed metal components reaching 90% of their melting temperature.

The need for efficient power-generating gas turbines has driven turbine designers to adopt all of the materials advances first introduced for aeroengines. In the largest gas turbines—nearly 0.5 gigawatt in size—the hottest components are cast as big single crystals from the same alloys used for their smaller aeroengine counterparts. These components also utilize thermal barrier coatings for added heat protection. Fractions of percent difference in combined cycle engine efficiency can sway a utility company's purchasing decisions. Clearly, in transportation and power generation using industrial gas turbines, materials lead the way in efficiency and a continued U.S. industry competitive advantage.

The critical role advanced materials play in energy security extends way beyond power generation and transportation. High-temperature superconductor and low-temperature fuel cell research within Los Alamos National Laboratory's (LANL's) Materials Science and Technology Division are two particularly relevant examples. High-temperature superconductivity has evolved tremendously to where commercial tape products are now available, but at a high price. The race for lower cost tape materials with higher current-carrying capacity has become a worldwide competition. Today's superconducting tapes are complex, layered structures and their successful application poses challenging materials and materials-processing milestones. Research underway at LANL is helping to answer fundamental questions about the interface structure, each layer's effect on the integrated system, and the merit of various processing routes.

Our fuel cell work mirrors the high-temperature superconductor research. Here too, materials challenges, which closely relate to product quality and cost, enable successful commercialization. Our research, built upon an almost 30-year development history of the polymer electrolyte membrane (low-temperature) device, centers on the expensive platinum materials required to catalyze the electrode reactions. We've invented processing routes to dramatically reduce the amount of platinum required, but ultimately we'd like to eliminate the platinum altogether. As with superconducting materials, we perform both basic, publishable research and collaborative research and development with industrial partners.

Just as an advanced aeroengine continues to amaze me, I am convinced I will someday board a maglev train riding on high-temperature superconductor rails, pass (perhaps unknowingly) a high-temperature superconducting transmission line, or purchase a fuel cell-powered automobile or home fuel cell power generation unit, and will marvel at the materials technologies that enabled these products. I'll also know that LANL's materials scientists significantly contributed to the eventual realization of these technological advances and to the continued worldwide leadership of U.S. industry.

Save it for a Rainy (or Windless, or Very Hot) Day

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vehicles, hydrogen and electric batteries, don't have nearly the same energy density as gasoline. Lower density means bigger, heavier, and/or more costly on-board storage systems. A future when zero-emission vehicles are powered by hydrogen and electricity produced from clean, domestic energy sources (solar, wind, hydro, biomass, nuclear, clean coal) may sound great, but it will never happen unless the energy storage problem is solved.

Los Alamos National Laboratory is working to make it happen with our world-renowned expertise in two scientifically challenging areas that show great promise for grid and transportation energy storage—superconductivity and hydrogen. Our relevant capabilities include

- Chemical and materials science
- Hydrogen utilization via fuel cells
- Advanced computing and analysis
- Superconductor development for flywheel and magnetic energy storage
- Advanced materials for flywheel and magnetic storage
- System analysis to explore combined storage/transport schemes such as liquid-hydrogen-cooled superconducting transmission lines.

This issue of *Los Alamos Energy Security* features some of the Laboratory's work in these areas. The ground-breaking efforts of Los Alamos's Superconductivity Technology Center and its industrial partners to produce record lengths of superconducting material will enable power applications that were never before possible. And with over 50 years of experience in advanced hydrogen systems and 28 years of innovation in fuel cells, no laboratory is better poised to make hydrogen storage and utilization a safe, efficient, and affordable part of the energy future.

> ***Storage functions as a "shock absorber" for the nation's electric infrastructure, enhancing its efficiency, reliability and security.***
>
> —Energy Storage Council White Paper (www.energystoragecouncil.org)

— Anthony Mancino and Greg Swift

The Challenge of Hydrogen Storage

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On-Board Hydrogen Storage: Key Factors for US DOE Targets

- Gravimetric Capacity (weight)
- Volumetric Capacity
- Storage System Cost
- Storage Material Cost
- Energy Efficiency of Recycle Process
- Speed to Fill
- Leakage
- Toxicity
- Safety
- Life Cycle

board the vehicle. Gasoline set a difficult standard to surpass for any alternative. This is the challenge facing hydrogen.

The development of an alternative transportation economy, such as a hydrogen economy, will require significant breakthroughs in a number of areas. Hydrogen does not occur free in nature in usable quantities, so it will need to be produced from other energy sources. There are two ways we can get it: (1) remove hydrogen from hydrocarbon fossil fuels; or (2) split H_2O to separate the H_2 (hydrogen) from the O (oxygen). The obvious drawback to the first method is that it relies on the very fossil fuels from which we eventually need to wean ourselves. The second method requires energy, so it must be fueled by renewables or nuclear power to be a clean solution for the future. Another inconvenient reality about hydrogen is that it takes as much energy to make, perhaps more due to conversion inefficiencies, than it will surrender when burned or passed through a fuel cell. However, none of these hard facts about hydrogen negate its value when it is seen for what it really is—an energy storage medium. Whether it relies on fossil fuels, nuclear power, or renewables with all their combined

> *Unlike hydrogen, gasoline is both an energy source and an energy carrier. It set a standard that will be difficult for any alternative to surpass.*

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The Chemical Hydrogen Storage Center of Excellence

Replacing petroleum-powered vehicles with hydrogen-powered vehicles requires a number of technological breakthroughs, but perhaps the greatest challenge is storing enough hydrogen on board to achieve an adequate driving range. Without adequate range, hydrogen-powered vehicles will be confined to major cities, and consumers will be less likely to relinquish gasoline-powered cars for hydrogen vehicles. To help meet this challenge, Los Alamos National Laboratory and several partners have come together to form the Chemical Hydrogen Storage Center of Excellence.

Chemical Hydrogen Storage Center Partners

Los Alamos National Laboratory

Pacific Northwest National Laboratory

Northern Arizona University

Pennsylvania State University

University of Alabama

University of California, Davis

University of California, Los Angeles

University of Pennsylvania

University of Washington

Intematix Corporation

Millennium Cell, Inc.

Rohm and Haas Company

U.S. Borax

The FreedomCAR and Fuel Partnership—a collaboration between the U.S. Department of Energy (DOE), the U.S. Council for Automotive Research, and energy companies—has developed on-board hydrogen storage targets with the goal of "achieving similar performance and cost levels as current gasoline fuel storage systems." In order to provide a 300-mile driving range between refueling without unacceptably bulky storage vessels, the DOE has established targets for year 2010 of storing 0.045 kilogram (kg) hydrogen per liter of storage system volume and 0.06 kg hydrogen per kg of storage system mass. Longer-term targets are even more demanding: 0.081 kg hydrogen per liter, and 0.09 kg hydrogen per kg of storage mass by the year 2015. The DOE has also established targets of 60% for the overall energy efficiency of storing hydrogen.

To put the storage density target numbers into context, note that compressed hydrogen gas at 200 atmospheres pressure is only 0.017 kg hydrogen per liter, and the pressure tank requires additional volume and mass. The greatest density of hydrogen that can ever be practically achieved is that of liquid hydrogen itself, only 0.07 kg per liter. Thus, compressed or liquefied hydrogen can never meet the DOE's 2015 target density.

Many researchers believe that the key to reaching, and even exceeding, the DOE target hydrogen storage densities is to store not pure elemental hydrogen, but instead hydrogen that is physically or chemically bound to materials that can be made to release the hydrogen under well-defined conditions. One such means of storing hydrogen is by using metals that react with hydrogen at room temperature to form a hydride phase and release the hydrogen when heated. Another such means of storing hydrogen is chemical hydrogen storage, where the chemically bound hydrogen is released not by heat alone, but by a more tangible chemical reaction or catalytic chemical process. One of the best-known means of chemical hydrogen storage is called Hydrogen On Demand™ by its developer, Millennium Cell, and involves the catalyzed reaction between sodium borohydride and water to release hydrogen and form sodium borate.

Even though hydrogen-storing materials and hydrogen-releasing reactions have been known for some time, none presently meets both the DOE storage density and energy efficiency targets. For example, while palladium hydride is a convenient means of storing hydrogen with good volumetric capacity, the weight capacity is only 0.019 kg H_2 per kg owing to the relatively high atomic weight of palladium, so much lighter elements must be used to meet weight targets. And while sodium borohydride ($NaBH_4$) is a convenient means of storing hydrogen with good volume and weight capacity, it is also a relatively expensive material whose industrial synthesis is energy-intensive making the energy efficiency of storing hydrogen in the form of $NaBH_4$, made by today's methods, less than 40%.

In 2003, the DOE issued the Grand Challenge storage call, asking for Centers of Excellence to develop new materials and processes that could meet all the targets for storing hydrogen. Three Centers of Excellence have been formed in response to this Grand Challenge. Sandia National Laboratories (California) and its partner institutions are working to develop reversible metal hydride storage materials that use light elements to meet the storage density targets. The National Renewable Energy Laboratory (Colorado) and its partner institutions are working to develop high-capacity hydrogen-sorbing materials based on carbon. Los Alamos National Laboratory, in partnership with the Pacific Northwest National Laboratory, 7 universities and 4 companies, is working to develop chemical hydrogen storage materials.

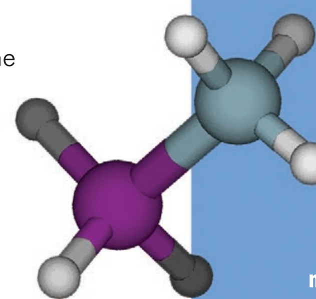
The Chemical Hydrogen Storage Center of Excellence, which started work in early 2005, is pursuing a multi-pronged research approach aimed at meeting DOE targets. Center partners are focusing on enabling the Hydrogen On Demand™ system by developing

continued on next page

THE IMPORTANCE OF BORON

The makers of 20 Mule Team® Borax like to advertise their product's many uses, from washing diapers to deodorizing garbage pails to preserving flowers, but "hydrogen storage medium for cars of the future" isn't on the list even though that may turn out to be borax's most important use yet. The element boron, which can be derived from the borax mineral, could be the answer to hydrogen storage.

An optimal chemical hydrogen storage system would have lots of chemically-combined hydrogen in a very light storage material, would allow the chemically-combined hydrogen to transform easily into hydrogen gas when needed, and should be unreactive (that is, hold on to the hydrogen) until needed. Boron materials meet these criteria remarkably well. Boron atoms form bonds with one, two, three, and even four hydrogen atoms, bonds that are kinetically stable but can be broken in favor of H-H bonds when conditions (catalyst, temperature, other reagents) are right. As for weight, Boron (number 5 on the periodic table of elements) is the lightest element, beside hydrogen itself, that bonds to hydrogen without a hazardous drawback. Helium (#2) is non-reactive and won't bond, lithium (#3) forms a hydride so dangerously reactive it can spontaneously ignite in damp air, and beryllium (#4) is toxic.



One of the most intriguing candidate materials for chemical hydrogen storage is ammonia-borane, NH_3BH_3, which is shown at left. The model shows 6 hydrogen atoms (gray) bound to larger boron and nitrogen atoms (image courtesy of Pacific Northwest National Laboratory). A white crystalline solid stable at room temperature, ammonia-borane normally begins to release hydrogen when heated to about 170-180°F. If all the hydrogen were released, it would be over 19% hydrogen, making it one of the highest-capacity hydrogen storage materials theoretically possible. But the material can undergo other reactions that release more than just hydrogen; depending on conditions it can also lose ammonia, borane, or borazine—volatile compounds that would quickly degrade a fuel cell—and it can form refractory ceramic products that are costly to recycle and regenerate. Several Center partners are actively working to develop catalysts and reaction conditions that facilitate the controlled release of hydrogen from ammonia-borane while preventing the formation of other volatile compounds and ceramic products. Other Center partners are studying different boron compounds which have lower storage capacity (still well above DOE targets) but which may release hydrogen without unwanted volatile side-products.

U.S. Borax's principal mine in the Mojave Desert. Boron is obtained naturally as oxides from large borax deposits, and borax resources are abundant enough to supply the world's hydrogen transportation needs. But energy-efficient methods must still be developed for borax conversion and for subsequent regeneration cycles. (Photo courtesy of U.S. Borax)

WHAT'S SO SPECIAL ABOUT CHEMICAL HYDROGEN STORAGE?

Diversity of options

There are a number of molecules, structures, and processes that could potentially meet the DOE targets and minimize system cost as well as address key aspects of system performance (e.g., on-board heat management).

A liquid or solid fuel infrastructure

Chemical hydrogen storage systems could be manufactured (or regenerated) at industrial-scale sites and transported to fueling stations in a liquid or solid form not unlike the current infrastructure used for transporting gasoline, thereby helping facilitate a transition to a hydrogen economy.

No handling of hydrogen by consumers

With a chemical hydrogen storage system, it is possible that hydrogen in the "hydrogen economy" could only exist transiently at the electrode of a fuel cell when needed. Refueling could involve transferring a liquid or solid hydrogen storage material rather than hydrogen itself, simplifying the refueling process.

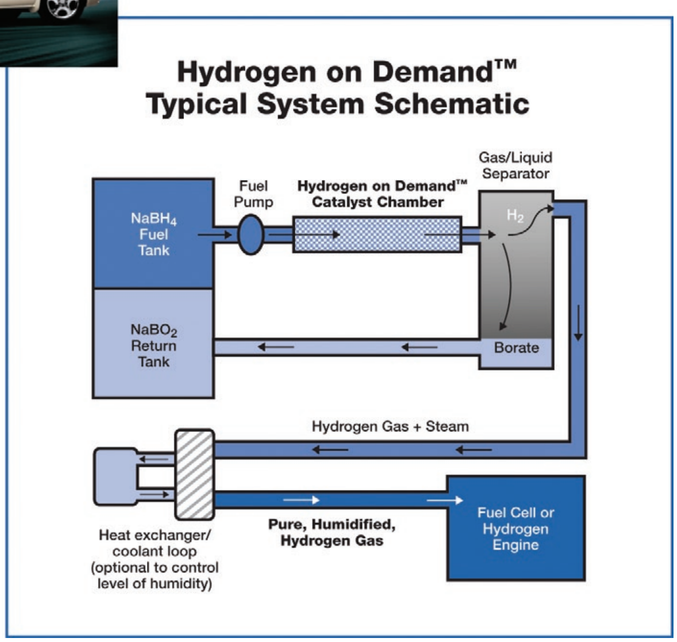
Industrial-scale regeneration away from the vehicle

Regeneration of spent hydrogen storage material will likely occur off-board at centralized facilities with economies of scale (to minimize costs) and industrial safety standards.

DaimlerChrysler's Natrium is a fuel cell research car that runs on Sodium Borohydride (photo courtesy of DaimlerChrysler). The diagram shows the Hydrogen On Demand™ fuel system developed by Millennium Cell.

In a typical system, a fuel pump directs fuel from a tank of sodium borohydride ($NaBH_4$) solution into a catalyst where the fuel solution generates hydrogen gas and sodium metaborate in solution. The hydrogen and metaborate solution separate in a second chamber, and the borate is returned to a collection tank. The hydrogen gas optionally can be processed through a heat exchanger to achieve a specified level of humidity and is then sent to the fuel cell or internal combustion engine for consumption (diagram courtesy of Millennium Cell).

new routes for regenerating sodium borohydride from the product sodium borate. Fundamental thermodynamic properties of sodium borohydride establish the maximum possible energy efficiency of storing hydrogen in this system as 70%, meeting the DOE efficiency target and considerably greater than the actual energy efficiency of the present manufacturing process. We are addressing the hard question by carefully scrutinizing what is known about sodium borohydride chemistry:

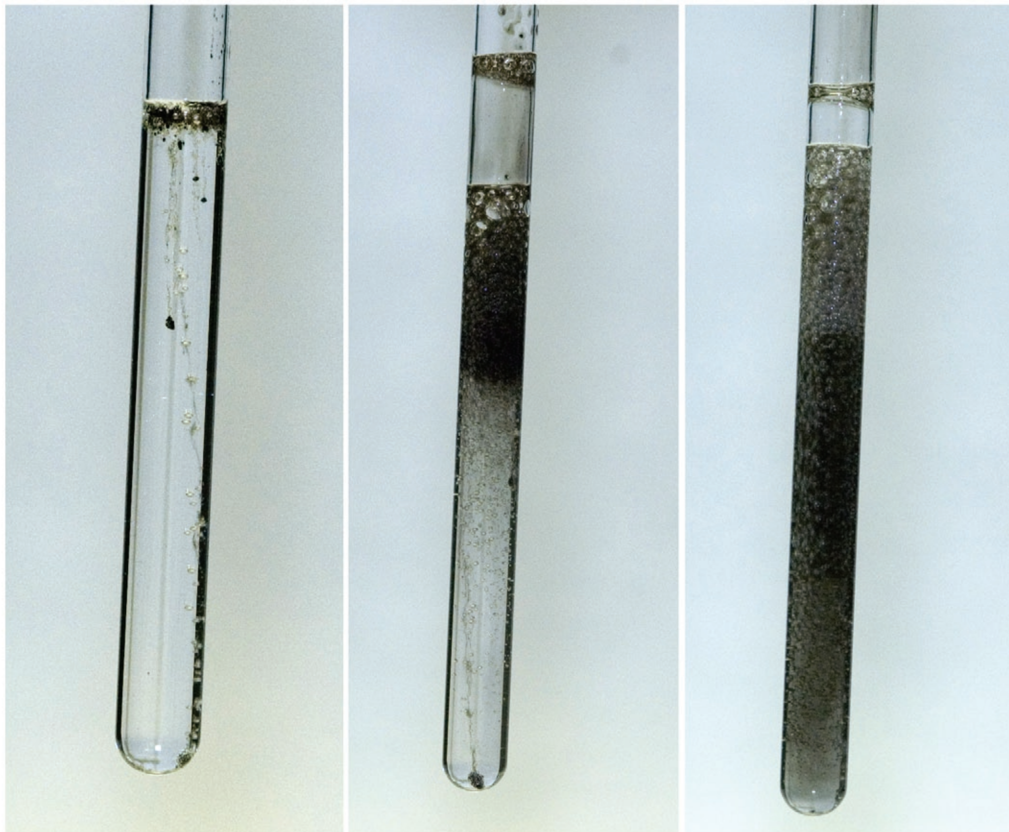


can we realistically expect to devise a new cost-effective manufacturing process that approaches 70% energy efficiency?

At the same time, the Center is pursuing a second tier of research aimed at developing the chemistry of other boron-hydrogen materials, materials that may provide an even greater density of stored hydrogen and more energy-efficient regeneration than sodium borohydride. We are also exploring how hydrogen can be stored using other reaction and material concepts, including novel organic compounds and reaction mixtures as well as nanostructured materials based on light elements. One of the new compounds under study can be seen in the series of images on the facing page (above right) where a quiescent liquid mixture (left) begins to evolve hydrogen immediately when particles of catalyst are added, leading to more rapid hydrogen evolution in a matter of seconds as the catalyst particles begin to disperse (center), and goes on to vigorous reaction (right). This occurs at room temperature, which is important to cost and efficiency.

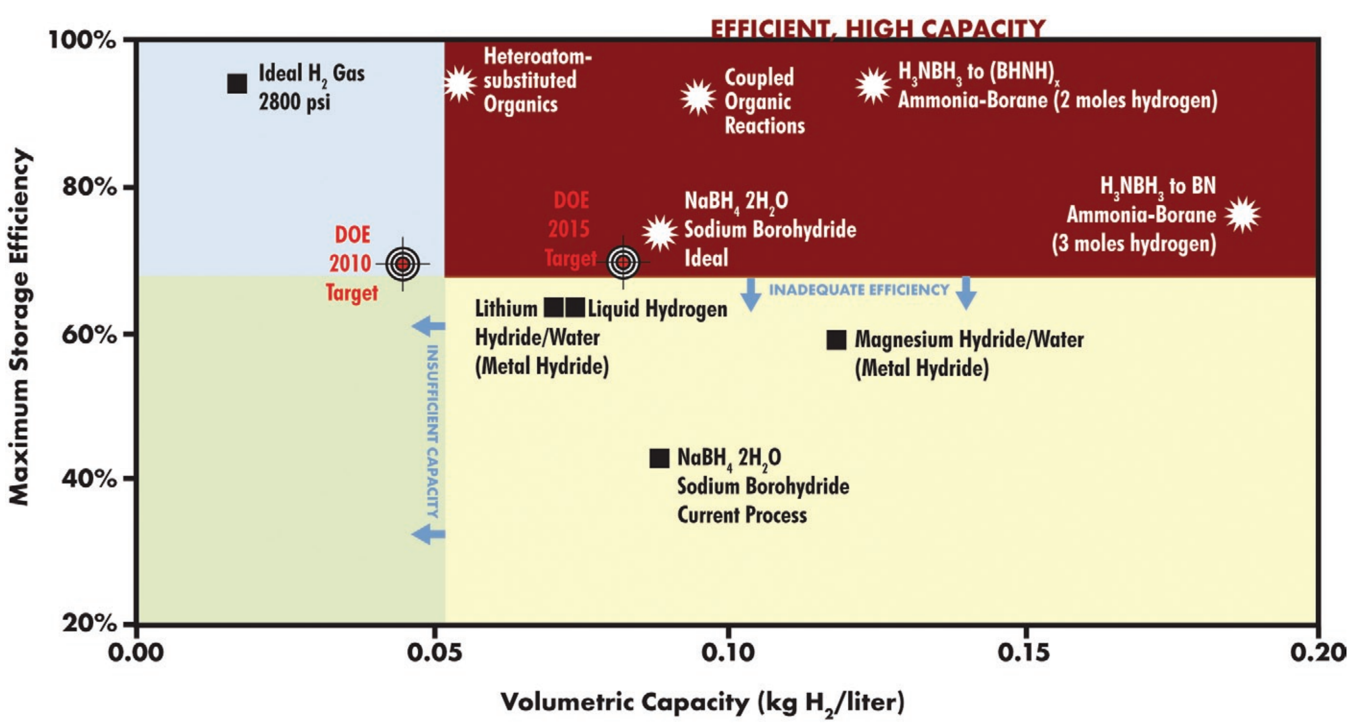
At this early stage the decisions for the Chemical Hydrogen Storage Center have focused on what materials and concepts to pursue. We have based our decisions on a combination of thermodynamic considerations and DOE target criteria. If a material or concept doesn't meet the year 2010 storage density target, and/or the fundamental thermodynamic properties of a material don't allow it to ever be 70% energy efficient in storing hydrogen, we have excluded it from the Center's research and development portfolio. Additional "go/no go" decisions will be made based on actual performance of different candidate materials as Center work progresses, and we anticipate that within 3 years we will have identified which of the initial concepts should be abandoned and which should be aggressively pushed into development.

— *David Thorn, Frances Stephens, Karl Jonietz, William Tumas, R. Tom Baker*



One of the new chemical compounds for hydrogen storage under development at Los Alamos. The quiescent liquid mixture (left) begins to evolve hydrogen immediately when particles of catalyst are added. More rapid hydrogen evolution occurs in a matter of seconds as the catalyst particles disperse (center) and proceed on to vigorous reaction (right), all at room temperature.

The hydrogen storage materials discussed in this article are represented in this plot showing maximum storage efficiency (defined as the ratio of energy stored as hydrogen to the total energy required to regenerate the spent storage material) as a function of the volumetric capacity (defined as the number of kg of hydrogen stored per liter of material). The Center's R&D targets are provided in the upper right zone where materials have the potential to meet both storage efficiency and capacity targets. (Note: The efficiencies plotted for these materials are the thermodynamically allowable maximum efficiency. R&D is necessary to realize efficiencies approaching these ideal values and to develop overall storage systems that meet the capacity targets.)



David Thorn

During the RECS summer school, students and instructors gather around a CO_2 injection well at KinderMorgan's SACROC facility in Snyder, TX.

Laboratory Conducts Summer School in CO_2 Sequestration

The science of carbon sequestration got some new recruits this summer as college students and early career scientists from across the country came to New Mexico to learn about this emerging field by participating in the Research Experience in Carbon Sequestration (RECS) program.

RECS was sponsored by the Department of Energy's Fossil Energy Program and hosted by Los Alamos National Laboratory and EnTech Strategies, a Washington, DC-based carbon sequestration consulting firm. The program was designed to align with the core elements of the DOE's carbon sequestration efforts. It was held over two weeks at the College of Santa Fe with field work at KinderMorgan CO_2's SACROC site, an enhanced oil recovery facility in Snyder, TX.

RECS is a first-of-its-kind, summer research program for undergraduates, graduates, and early career professionals interested in the technologies, theory, economics, and novel approaches involved in capturing CO_2 in geological settings. Experts from academia, industry, and government laboratories presented information on CO_2 separation, capture, long-term storage, monitoring, and mitigation.

The RECS program is a follow-up to last year's US-Norway program on carbon capture and geologic storage, which was a collaborative effort between the National Energy Technology Laboratory, DOE's Office of Clean Energy Collaboration, and the Norwegian Research Council. That 10-day program, also hosted by Los Alamos National Laboratory, was held in Santa Fe, NM for 20 participants from Norway and the U.S. Next year's RECS 2006 is already in the planning stage.

Los Alamos Scientists May Influence Climate Change Policy

On July 21, 2005, the Scripps Howard News Service reported that "Senate Energy Committee Chairman Pete Domenici today was to begin a series of hearings on global climate change that mark his conversion from a skeptic to an advocate for doing something … about the problem." Domenici said he became convinced that something should be done about the human impact on climate after being briefed by scientists at Los Alamos National Laboratory. That briefing was provided by Jim Bossert and George Guthrie of the Earth and Environmental Sciences Division and Phil Jones and Ken Eggert from Theoretical Division.

After senators failed to agree on greenhouse gas limits in the energy bill, Domenici promised Senator Jeff Bingaman, the ranking Democrat on the energy committee, that he would hold hearings on climate change. Bingaman believes that the hearings will lead to a legislative proposal. Domenici acknowledged the possibility but warned that the hearings will still include many skeptics. Los Alamos' Associate Director for Strategic Research, Terry Wallace, Jr., said "this is a wonderful example of LANL expertise making a difference in the policy world."

Senators Pete Domenici (left) and Jeff Bingaman, both of New Mexico.

Los Alamos Scientist Appointed Adjunct Science Team Member to DOE's Atmospheric Science Program

Manvendra Dubey, of Los Alamos' Earth and Environmental Sciences Division, has been appointed an Adjunct Science Team Member of DOE's Atmospheric Science Program (ASP). The ASP, part of the Office of Science, is a $15-20M/yr program focused on reducing uncertainties in climate effects of anthropogenic aerosols. This is a sister program to DOE's Atmospheric Radiation Monitoring (ARM) program with much synergy between them.

The ASP program coordinates a variety of multi-agency field campaigns to focus on key questions. One such campaign is ongoing in California to study marine stratus clouds, and another will happen in Mexico City next year. Dubey's team will be measuring

The Challenge of Hydrogen Storage, continued from page 3

shortcomings, it still allows us to store energy for use at another time, which is important to the stability of the electric grid, or in another place, which is critical to transportation.

But there's another hard reality clouding the hydrogen future. While hydrogen is good at storing energy, there's still no real good way to store hydrogen. Perhaps the greatest challenge for a hydrogen economy is on-board hydrogen storage. Hydrogen's advantage of high energy content on a weight basis is offset by its low density (weight per unit volume). If vehicle range is not to be compromised, it will be necessary to develop innovative concepts for storing enough hydrogen on board vehicles. On-board hydrogen storage must also be made available at reasonable costs and energy efficiencies, thereby putting significant constraints on new materials and processes.

A number of hydrogen storage concepts have been advanced over the years, including compressed gas, cryogenic liquid, physical adsorption on porous materials (including carbon nanotubes), or chemical binding within metal hydride or other chemical frameworks. Each has advantages and disadvantages. To date, no perfect solution has been discovered; all of the mature systems fall short on one or more of the DOE targets.

Los Alamos National Laboratory is one of two national laboratories leading the DOE's Chemical Hydrogen Storage Center of Excellence, which is tasked with meeting the challenge of hydrogen storage by developing chemical systems where hydrogen is released through a chemical reaction. Los Alamos has a long history and broad range of capabilities in hydrogen stemming from its defense work. This new initiative complements our work in hydrogen fuel cell development for which Los Alamos holds several seminal patents and is the most-cited laboratory in the world. In this issue of *Los Alamos Energy Security*, you can learn more about the Hydrogen Storage Center of Excellence and Los Alamos' research into the use of clathrate hydrates for hydrogen storage.

— *William Tumas, Karl Jonietz, Anthony Mancino, Greg Swift*

Manvendra Dubey of Los Alamos' Earth and Environmental Sciences Division.

black carbon during these campaigns. The campaigns will be generating a wealth of data on air pollution, cloud properties, and radiation that will be invaluable for testing and validating processes in climate models.

Los Alamos Fuel Cell Researchers Honored for the Most Significant R&D Contribution of the Year

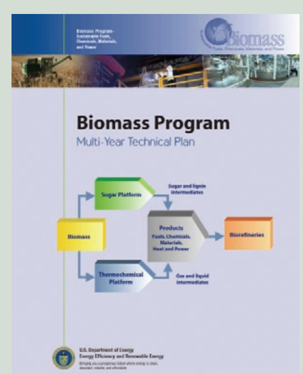
DOE's Office of Hydrogen, Fuel Cells and Infrastructure Technologies (OHFCIT) honored Rod Borup, a Team Leader in the Materials Science and Technology Fuel Cell Program, for the most significant R&D contribution of the year for his team's work in fuel cell durability. JoAnn Milliken, Chief Engineer of OHFCIT, noted the importance of testing initiated by Los Alamos National Laboratory under simulated automotive drive cycles, the development of accelerated test methods, and the scientific excellence shown in determining and disseminating the underlying causes of performance degradation. Borup expressed appreciation for the contributions of team members John Davey, Fernando Garzon, Mike Inbody, and David Wood.

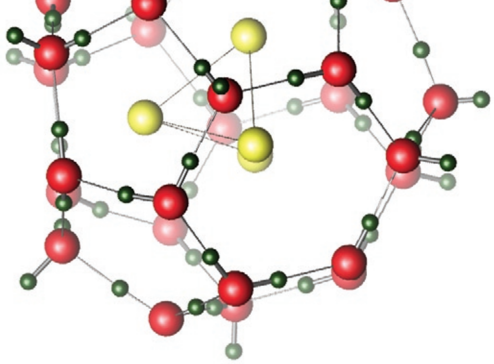
Los Alamos Team Begins Energy from Biomass Project

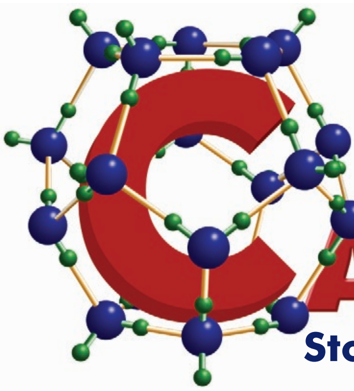
Cathy Gregoire Padró, Project Leader for Hydrogen Systems in the Materials Science and Technology Division, has been awarded a new program start from DOE's Office of Energy Efficiency and Renewable Energy for a one year, million-dollar project for Biomass Assessment Tools ($1M for the first year, including a $220K subcontract to the University of Illinois). The planned research supports needs outlined in DOE's Office of Biomass *Multi-Year Technical Plan*, including development and analysis of an "Innovative BioSyngas Production Process."
This process work will pursue new low-temperature, low-pressure process chemistries to produce syngas with high selectivity from oligosaccharide mixtures as an intermediate step. The task will then move toward catalytic systems designed to convert the more difficult, higher molecular weight, less reactive cellulosics directly, followed by mixtures containing lignin and hemicellulosics. If successful, direct aqueous reforming of oligosaccharides and cellulosics would be an enabling technology for future integrated biorefineries.

The project leverages Los Alamos successes and DOE investments in catalysis and hydrocarbon fuel processing. Cathy Padró will lead the assessment task, with work on process chemistries performed by Kevin Ott (Chemistry Division), Rod Borup (Materials Science and Technology), and additional scientific, technical, postdoc, and student support.

The Los Alamos biomass project will support needs outlined in DOE's Office of Biomass *Multi-Year Technical Plan*, which can be downloaded at http://www.eere.energy.gov/biomass.

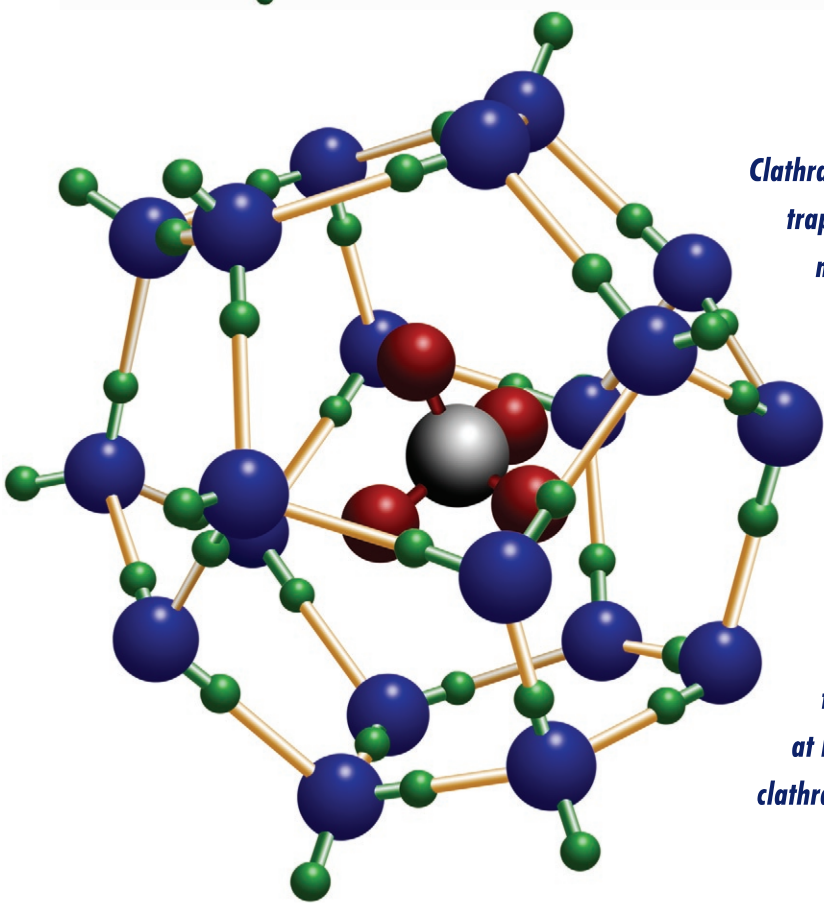






CAGED ENERGY

Storing Hydrogen in Clathrates

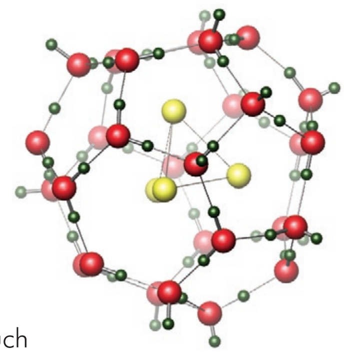


Clathrates are formed when molecules of one compound become trapped within the cage structure of another compound. The most common clathrates are gas hydrates which consist of gas molecules—such as methane, ethane, propane, isobutene, and carbon dioxide—trapped inside a cage-like lattice of ice. Huge reserves of naturally occurring methane hydrates are present in permafrost regions and on the ocean floor where the low temperatures and high pressures necessary for clathrate hydrate formation exist. The importance of these compounds cannot be overestimated because of their ability to condense and thereby store vast quantities of trapped gas. Researchers at Los Alamos are now studying ways to apply this feature of clathrates to hydrogen storage.

Methane hydrates are a clathrate that form in abundance on the ocean floor and in permafrost regions. In the model above, a CH_4 methane molecule (red and gray) is trapped inside a solid lattice of frozen H_2O (green and blue). Clathrates can condense and store a vast amount of gas. For example, one cubic meter of methane hydrate can contain as much as 180 m^3 of methane. Researchers at Los Alamos are now trying to exploit this clathrate characteristic to store hydrogen.

The unique behavior of clathrates and their ability to enhance energy and water security have long been recognized by scientists at Los Alamos who have been studying them as a vast domestic source of naturally occurring methane fuel, as a potential host to store carbon dioxide generated by fossil fuel combustion, and as a medium for trapping and removing salt from seawater or saline aquifers. However, recent experiments at Los Alamos, in collaboration with researchers from the Carnegie Institution of Washington, have led to a surprising clathrate discovery. Hydrogen atoms, once thought to be too small to support a clathrate structure, were observed filling small cavities in a lattice of frozen water molecules. Unlike other clathrates, in which only one gas molecule occupies each cavity, the hydrogen atoms clustered into groups of two or four. The hydrogen clathrates also remained stable at ambient pressure and at higher temperatures than expected. These discoveries, combined with the large gas storage capacity of clathrates, may have important implications for hydrogen storage, which is one of the key technical challenges facing a future hydrogen economy.

The best way to understand clathrates is to "watch" them in action, and Los Alamos has a number of unique experimental facilities that allow that to happen. A newly developed pressure cell allows researchers to combine experimental techniques—such as neutron diffraction, ultrasonic interferometry, Raman and infrared spectroscopy—to characterize the physical properties of clathrates at the high pressures and low temperatures required for their formation. Neutron diffraction studies at the Los Alamos Neutron Science Center (LANSCE) have given researchers an unprecedented glimpse into the inner structures of clathrates. Using neutron diffraction, a beam of neutrons passes through a material under study and scatters into a pattern that reveals the relative positions of the atoms in the target material. For gas-hydrate clathrate studies, neutron diffraction offers some advantages over other experimental methods, such as X-ray diffraction. Neutrons can "see" into enclosed metal pressure vessels in real time to show crystal chemistry, formation kinetics, and phase transitions associated with sequential emptying of the cages. In addition, neutrons can pinpoint with extreme accuracy the positions of even the smallest atoms—hydrogen atoms.



Clathrates exhibit characteristics that could make them an ideal medium for on-board hydrogen storage. Initial studies show a comparatively high energy density of 5.23 wt% (i.e., the hydrogen fuel accounts for 5.23% of the weight of the storage medium, in this case ice, and hydrogen combined). The Department of Energy's technical objectives for 2010 and 2015 are 6 wt% and 9 wt% respectively, so even at this early stage of development, clathrates are not far from the 2010 objective. Fast kinetics of clathrate formation and easy reversibility are also important. The former presented a problem until Los Alamos researchers developed an extremely rapid method for hydrogen clathrate synthesis. This method, which has a patent pending, has reduced the time for clathrate formation from several hours to less than 10 minutes. Release of the trapped gas simply requires controlled melting of the ice. Hydrogen clathrates are also a far safer storage medium than a tank of highly compressed gas under the backseat of your car.

While the pressure and temperature requirements for hydrogen clathrates are more promising than expected, they are still impractical for on-board storage. In nature, as mentioned earlier, clathrates form on the ocean floor where temperatures are low and pressures high. To address this problem, researchers are studying an expanded family of molecular inclusion compounds, including clathrasils, cryptates, and metal-organic frameworks. These compounds, like clathrates, are formed by a host-guest relationship, but unlike clathrates, they are stable at ambient conditions. Hydrogen clathrates, however, only remain stable at ambient pressure if their temperature does not exceed 145 K (-199°F). An understanding of a broader range of molecular inclusion compounds could allow researchers to fine-tune molecular structures. To increase the hydrogen load and achieve accessible pressure and temperature conditions, Los Alamos researchers are taking two molecular engineering approaches: (1) inserting additives to stabilize the crystal structure, and (2) modifying the host framework (i.e., the "cage") to tolerate large molecular distortions. It will be invaluable for hydrogen fuel applications to engineer innovative inclusion compounds of nano-porous cage/channel structures with superior properties

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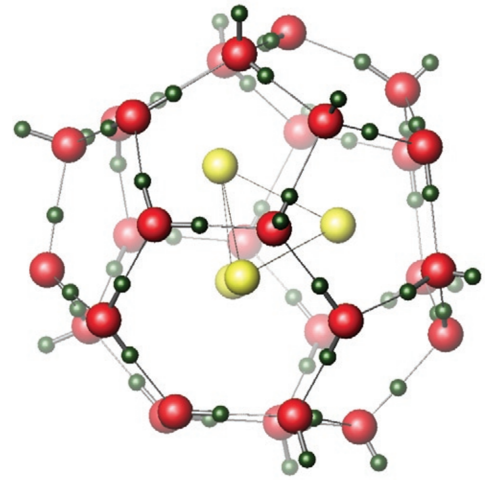
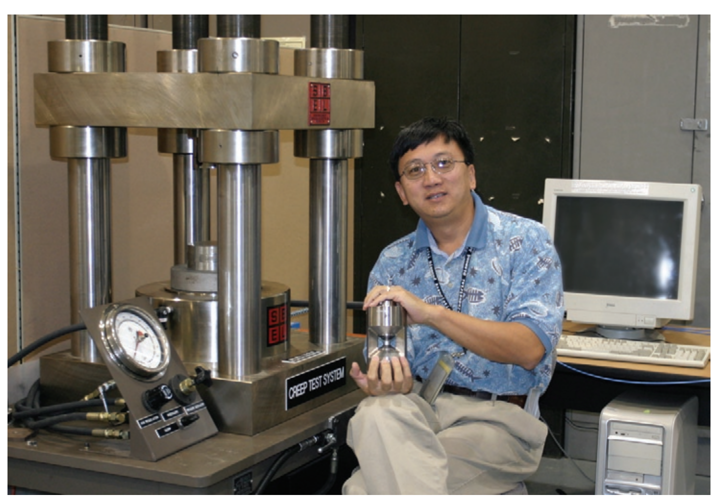


Hydrogen atoms were once thought too small to support clathrate structures, but recent experiments at Los Alamos have shown that to be untrue. In addition to forming stable clathrates, the hydrogen atoms (yellow spheres above) clustered inside the cages in groups of 2 to 4 and at extremely short distances from each other making them denser than the atoms in solid hydrogen. (Lokshin, K.A. et al. *Physical Review Letters*, vol. 93, no. 12, 2004, 125503)

Yusheng Zhao, Principal Investigator for clathrate studies at the Los Alamos Neutron Science Center, holds the ZAP cell that allows clathrate analysis through neutron diffraction.



Superconducting Magnetic Energy Storage

Improved grid reliability, better integration of renewables, and cost-effective response to peak demand

Superconductivity is one of those properties of metals that seem to make no sense. A typical metal wire, such as one made from copper, carries electrical current as do superconductors, but because of the wire's resistance the electrical current dissipates energy as heat. In 1911 at Leiden in the Netherlands, a student made the first measurements of mercury wire at the boiling point of liquid helium. When this student reported to his professor, Heike Kamerlingh Onnes, that the mercury wire had a resistance of zero Ohms, he was sent back to the lab to "do the experiment correctly." Subsequent experiments showed that the mercury wire really did have zero resistance. If the wire was formed into a closed loop or ring, current induced into the loop with a magnetic pulse showed no visible change even after several days; if the loop were made of a copper wire, the current dissipated in a fraction of a second. Superconductivity had been discovered, but these early superconductors only achieved zero resistance at the very chilly temperature of liquid helium (-452°F).

In the 1980's, a new class of superconductors were discovered which had zero resistance when cooled to the relatively higher temperature of liquid nitrogen (-321°F). These materials were oddly called "high-temperature superconductors." With this discovery, the economics of superconductors suddenly became much more attractive. It is said that while liquid helium costs as much as a good whisky, liquid nitrogen is cheaper than milk. Nature wasn't being completely cooperative though, for the new high-temperature materials are not simple metals but ceramics that are difficult to make into long wires. The Superconducting Technology Center at Los Alamos National Laboratory has been leading the effort to develop wires from these ceramics and, along with several other labs in the U.S. and other countries, has developed these materials to achieve conductors 1cm wide and 0.2mm thick carrying currents of over 1000A with no resistive heating.

If a magnet coil is formed from a superconducting wire and a field generated by passing current into the coil, that magnetic field can remain stable for long periods of time. This is one reason for the success of superconductors in MRI machines where a large, constant field is required. There is energy associated with a magnetic field and the energy density in and around the magnet scales as the square of the magnetic field. The total energy stored in an MRI magnet could be as high as 5 MJ—enough energy to run a 1kW electric kettle for over an hour. It is clear from this simple example that superconducting magnets could in principle be used to store large amounts of electrical energy in compact devices leading to the idea of Superconducting Magnetic Energy Storage (SMES). Between the discovery of low-temperature and high-temperature superconductors, designs for SMES were proposed to solve the emerging problem of how to store utility-scale amounts of electrical energy, culminating in suggestions for magnets kilometers in diameter storing the equivalent of the output of a large power station for a number of hours. The need to cool with liquid helium and the complexity of the resulting cooling system meant that an economy of scale gave the large systems the best chance of economic success. In the end, even these systems proved to be not viable and none were ever built. Superconducting materials could possibly be used to make local or neighborhood SMES systems, which could store around 100 kilowatt-hours of energy. This scale of SMES was very unattractive when it needed liquid helium for cooling but becomes very feasible at liquid nitrogen temperatures.

But why should we want to store this amount of energy? There are engineering and economic reasons. From an engineering perspective, the electrical delivery system is not always fully utilized. Demand peaks at certain times, but most of the time the transmission and distribution system operates well below this peak power value. Although this peak may only occur for a few hours during a year, the system has to be designed to transmit the peak power. If we were able to store some energy locally during off-peak times, the transmission system could be designed for lower peak powers. In practice, in the growing U.S. system this means we could put off upgrading cables and transformers for some time. A further engineering advantage is increased reliability; adding local storage effectively builds operating margin into a system at peak times. If something, somewhere fails, the operators have more options for maintaining supply.

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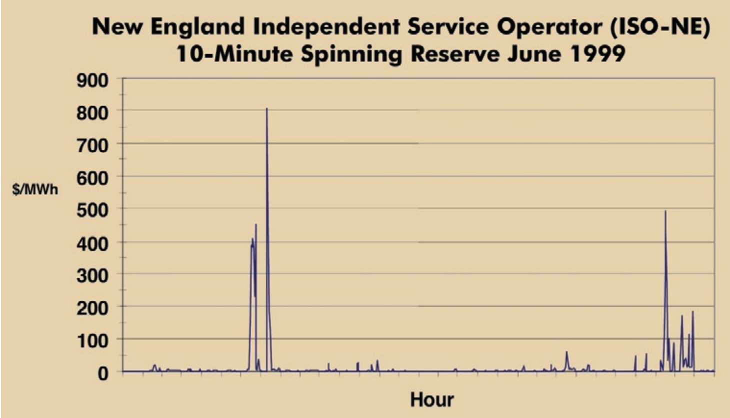
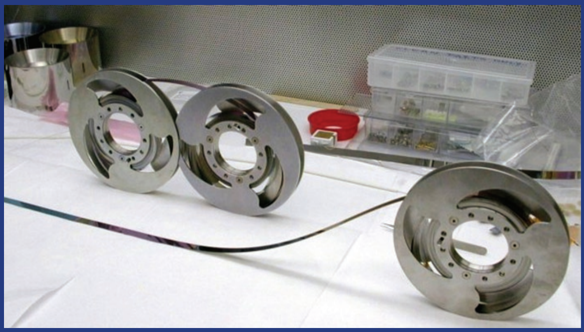


"During June 1999, an early heat-wave caught members of the New England ISO with numerous assets offline for maintenance. The resulting strain on ancillary services is indicated by the above chart, showing hourly prices for 10 minute spinning reserve during this month. The peak price of over $800/MWh is 800 times greater than the median price of $1.00/MWh and 70 times greater than the average price of $11/MWh" (*Transmission Reliability Multi-Year Program Plan, FY 2001 – 2005*, Office of Power Technologies, Energy Efficiency and Renewable Energy, U.S. DOE, 2001, p. 19). While this fluctuation is extreme, it does give some idea of the economic possibilities provided by an energy reserve stored in short-term superconducting storage.

WHAT'S LOS ALAMOS DOING ABOUT SMES?

The Superconductivity Technology Center (STC) at Los Alamos is supporting the development of SMES by developing high-temperature superconductors capable of carrying the currents required in the magnetic fields needed for energy storage. The nano-particle doped conductor disclosed by a team of STC researchers is ideal for this application.* This technology inserts nanometer-sized impurities into an otherwise "clean" superconductor. An external magnetic field trying to move into the conductor gets entangled on these nano-particles and the conductor retains its current-carrying capability to higher magnetic fields. This high-field conductor has been demonstrated in short lengths, and the STC team is now working to show continuous manufacturing routes for this material. When the magnetic field or current in a superconductor changes (i.e., when energy is taken from or put into the SMES device) some heat is generated. It is important to minimize this heating for both engineering and economic reasons, so the STC is pursuing "low loss" conductors and coil designs that will impact SMES development. The STC is working with the companies IGC-Superpower and American Superconductor to develop high current, low loss conductors and has a goal of producing test lengths of 1000A, 1cm wide conductors by FY 2006. Under the auspices of the Power Delivery Research Initiative contained in the Energy Bill recently signed by the President, the STC is funded to develop a test center in FY 2006 where machines, such as local SMES devices, can be tested under conditions relevant to utility use.

Reels of superconducting tape. Perhaps the greatest challenge in high-temperature superconductivity is creating lengths long enough for practical applications. Los Alamos and its industrial partners have achieved record lengths.

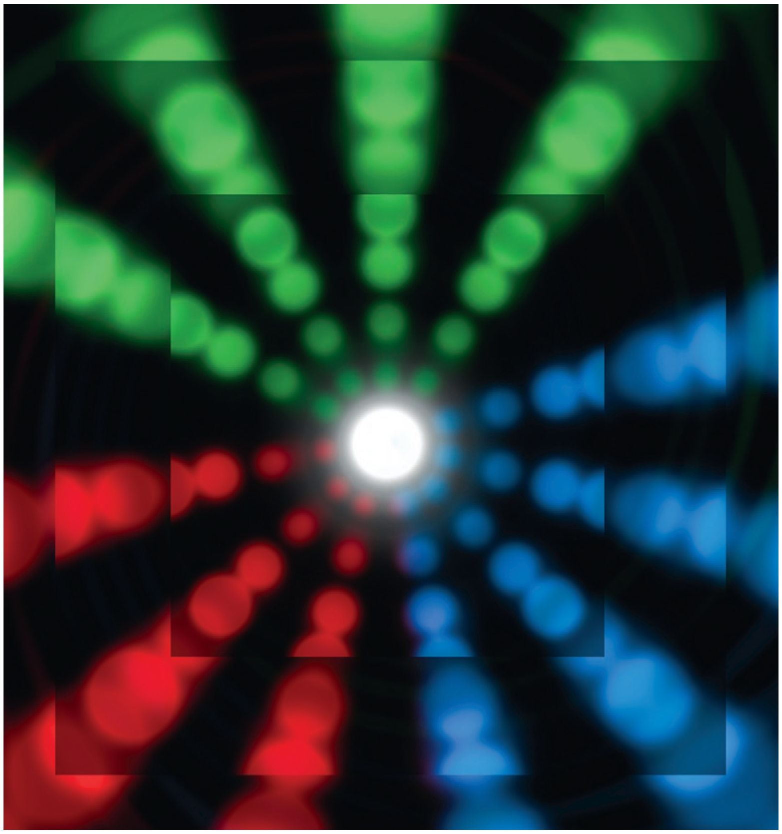


* "Strongly enhanced current densities in superconducting coated conductors of $YBa_2Cu_3O(7-x) + BaZrO_3$." Macmanus-Driscoll, J.L.; Foltyn, S.R.; Jia, Q.X.; Wang, H.; Serquis, A.; Civale, L.; Maiorov, B.; Hawley, M.E.; Maley, M.P.; Peterson, D.E. *Nature Materials*; v.3, no.7, p.439-443 (2004).

Scientists Develop Novel Multi-Color Light-Emitting Diodes

A team of University of California scientists at Los Alamos National Laboratory has developed the first completely inorganic, multi-color, light-emitting diodes (LEDs) based on colloidal quantum dots encapsulated in a gallium nitride (GaN) semiconductor. The work represents a new hybrid approach to the development of solid-state lighting. Solid-state lighting offers the advantages of reduced operating expenses, lower energy consumption, and more reliable performance.

In research published in the scientific journal *Nano Letters*, the team reports on the first successful demonstration of electroluminescence from an all-inorganic, nanocrystal-based architecture where semiconductor nanocrystals are incorporated into a p-n junction formed from semiconducting GaN injection layers. The new LEDs use a novel type of color-selectable nanoemitter, colloidal quantum dots, and make use of emerging GaN manufacturing technologies.



The first completely inorganic, multi-color LEDs could lead to energy-efficient, solid-state lighting.

According to Victor Klimov, who leads the nanocrystal-LED research effort, "numerous technologies could benefit from energy-efficient, color-selectable, solid-state lighting sources ranging from automotive and aircraft instrument displays to traffic signals and computer displays. Semiconductor nanocrystals, known also as quantum dots, are attractive nanoscale light emitters that combine size-controlled emission colors and high emission efficiencies with chemical flexibility and excellent photostability. The use of nanocrystals in light-emitting technologies has, however, always been hindered by the difficulty of making direct electrical connections to the nanocrystals. By putting the quantum dots between GaN injection layers, we've gotten around this difficulty."

The secret to making the electrical connection to the quantum dots is the use of a technique developed by a Los Alamos team specializing in advanced nanoscale processing. This technique uses a beam of energetic, neutral nitrogen atoms to grow GaN films. The technique, called ENABLE (for Energetic Neutral Atom Beam Lithography/Epitaxy), allows for the low-temperature encapsulation of nanocrystals in semiconducting GaN without adversely affecting their luminescence properties. By encapsulating one nanocrystal layer or two layers of nanocrystals of different sizes, the researchers have demonstrated that their LEDs can emit light of either a single color or two different colors. The two-color operation regime is an important step toward creating devices that produce white light.

First Examples of Base Metal Catalysts for Amine-Borane Dehydrogenation

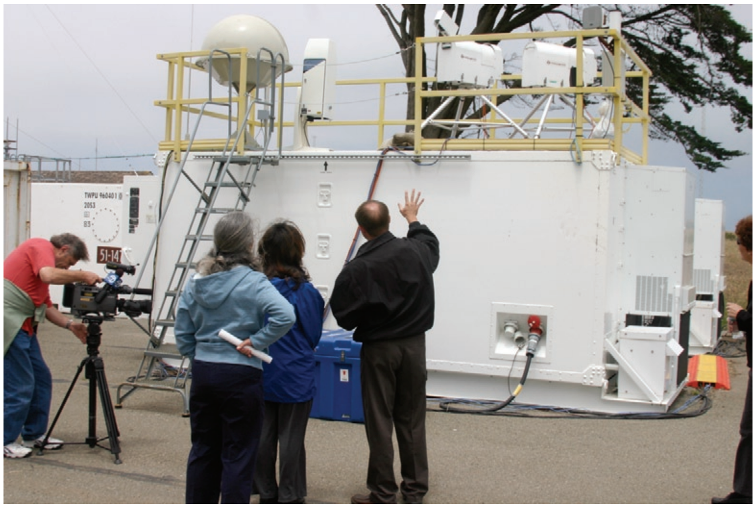
Ammonia-borane (AB, H_3N-BH_3) has been identified as a promising candidate for chemical hydrogen storage for transportation applications with a theoretical maximum material capacity of greater than 19 wt% hydrogen. While others have identified precious metal catalysts that release hydrogen from AB under mild conditions, a Los Alamos Chemistry Division summer student, Johanna Blacquiere, working with Rich Keaton and Tom Baker, recently discovered the first examples of inexpensive base metal (iron, nickel) complex catalysts for amine-borane dehydrogenation. A patent disclosure has been filed, and Blacquiere's poster won one of two best chemistry poster awards at this year's Student Symposium at Los Alamos. She will begin graduate school in chemistry at the University of Ottawa this fall.

Materials Science & Technology Team Reports Highest Recorded Performance for Fuel Cell

Researchers at Los Alamos' MST Division have published the highest reported performance for a direct methanol fuel cell. Improvements are based on a novel hydrocarbon membrane that offers the promise of lower cost systems for portable power applications. Y. S. Kim et al., *Journal of the Electrochemical Society*; 2004; v.151, no.12, p. A2150-A2156.

ARM Mobile Facility Deployed in Point Reyes, CA to Help Improve Global Climate Models

The Atmospheric Radiation Monitoring (ARM) Mobile Facility (AMF) was recently deployed in Point Reyes, California. The AMF is a high-profile climate monitoring facility designed to be employed anywhere in the world, specifically in under-sampled areas of scientific interest. The purpose of the facility is to collect long-term, continuous, quality data for use in improving global climate models. In collaboration with the U.S. Office of Naval Research and DOE's Aerosol Science Program, the objectives of the Marine Stratus, Radiation, Aerosol and Drizzle project at Point Reyes are to make observations of cloud aerosol interactions and improve understanding of cloud organization often associated with patches of drizzle. The AMF will contribute significantly to the scientific objectives of this project by providing state-of-the-art active and passive remote sensors to measure the detailed microphysical structure of drizzle patches and the associated clouds as they move ashore.



The Atmospheric Radiation Monitoring Mobile Facility collects data to improve global climate models.

The AMF will collect data for seven months at Point Reyes before being packed up and transported to its next assignment in Niamey, Niger to participate in the international African Monsoon Multidisciplinary Analysis (AMMA) Intensive Operational Period (IOP) in 2006. The AMF is deployed, operated, and maintained by Los Alamos' TWP/AMF Management Office team in the Earth and Environmental Sciences Division.

Caged Energy, continued from page 11

in selective separation, reversible encapsulation, fast kinetics, and high storage capacity of guest molecules.

While it's too early to tell what an engineered on-board hydrogen clathrate fuel system would look like, it's conceivable that one day hydrogen atoms—generated perhaps by solar, wind, or nuclear power—caged inside ice molecules could power your fuel cell vehicle. As you drive, the melting ice cages would release the hydrogen into the fuel cells until only water remained. You could then stop for rapid hydrogen clathrate regeneration in your tank, or simply pop out the spent container and exchange it for a fresh canister of caged energy.

— Yusheng Zhao and Anthony Mancino

Superconducting Magnetic Energy Storage, continued from page 13

Another engineering and economic issue has arisen with the advent of significant amounts of solar or wind energy on a grid which fluctuates in supply over periods of seconds as clouds pass in front of the sun or the wind drops. This drop in supply must be picked up instantly by another source. Without some way of storing easily available energy, utilities must keep conventional generators spinning, essentially storing energy in the rotating mass of the generator since no other storage mechanism reacts fast enough. This is not an attractive solution from an economic point of view. A SMES system is ideal for storing energy from renewable sources to smooth out short time-scale variations in output.

From an economic perspective, the cost of electricity is dominated by the market, in particular the difference between supply and demand. Domestic customers pay an average price, and suppliers buy electricity on the market. There are various types of contracts: a vendor might predict demand and buy a day ahead or even months ahead, or if unforeseen events arise they may need to purchase electricity just hours in advance. The shorter the time scale, the higher the fluctuations in price. The graph on page 13 shows an example of the short-term fluctuation in electricity prices. While the magnitude of the fluctuation shown is extreme, it does give some idea of the economic possibilities for short-term superconducting storage.

— Stephen P. Ashworth and Fred M. Mueller

ENERGY RESOURCES

Publications, events, and websites for people interested in energy-related issues.

Publications

U.S. Climate Change Technology Program

http://www.climatetechnology.gov/vision2005/cctp-vision2005.pdf

The Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan

http://www.eere.energy.gov/hydrogenandfuelcells/mypp (Section 3.3 covers hydrogen storage.)

National Electric Delivery Technologies Roadmap

http://www.electricity.doe.gov/about/vision.cfm
(Chapter 3 addresses electricity storage and superconductivity.)

Basic Research Needs for the Hydrogen Economy (DOE's Office of Science)

http://www.sc.doe.gov/bes/hydrogen.pdf

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Events

GHGT-8: 8th International Conference on Greenhouse Gas Control Technologies

June 19-23, 2006
Trondheim, Norway
http://www.ghgt-8.no

The main themes of GHGT-8:

- Policy initiatives and options to reduce greenhouse gas emissions
- Reducing greenhouse gas emissions from industry
- Capture, transmission, and storage of CO_2
- Developments in low emission power generation technology
- Low carbon energy carriers and the role of CO_2 capture and storage in their development
- Comparison of different options for greenhouse gas reduction

Websites

Department of Energy's Hydrogen Program http://www.hydrogen.energy.gov
DOE's portal to hydrogen programs, including access to several hydrogen roadmaps and plans in PDF format. See the link for hydrogen storage on the left.

Energy Storage Council http://www.energystoragecouncil.org
While this site is not Mac-friendly and could use updating, it still contains some interesting articles on energy storage. Click on the "About Storage" link near the top of the page.

Renewable Resource Data Center http://rredc.nrel.gov
Provides information on several types of renewable energy resources in the United States in the form of publications, data, and maps.

www.lanl.gov/energy

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